"Optical limiting via nonlinear scattering with solgel host materials."

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ABSTRACT

We describe studies of optical limiting by thermally induced nonlinear light scattering in highly porous solgel glasses. We impregnate the porous glass with a solution of reverse saturable absorber in a solvent that is index-matched to the solgel matrix at room temperature. We observe a strong enhancement of the limiting properties at high energies in the porous glass, compared to the performance of the reverse saturable absorber alone. We attribute this effect to nonlinear scattering. However, the properties of this scattering are substantially different to what was originally expected. We provide evidence that the observed effect is due to formation of gas bubbles in the focal region of the laser beam. These bubbles are trapped in the host matrix, allowing the effect to accumulate over several laser shots.

1. INTRODUCTION

Optical limiting by nonlinearly induced light scattering has been demonstrated in a number of systems. The most widely studied example is the strong optical limiting seen in liquid suspensions of amorphous carbon particles (dilute ink). The effect has been attributed to scattering and absorption by microplasmas formed after thermionic emission from heated particles of carbon.[1] An alternative explanation is that micro bubbles are formed due to the heating of the particles, and these bubbles scatter the beam.[2] Similar behavior has been observed in other clusters which show identical scattering dynamics to the carbon black suspensions (CBS).[3] Another approach to nonlinear scattering was introduced by Justus *et. al.*[4] who showed that limiting could be produced by immersion of a strongly scattering transparent medium in an index-matched liquid. If the temperature is changed, the index matching is degraded, and the composite medium scatters light, reducing the transmittance. By adding some absorbing dye to the liquid, the temperature change can be induced by an incident laser pulse. Hence, for low laser power, where the heating is small, the composite medium is highly transparent, while at high power a large temperature change is induced, causing the transmittance of the laser to be small. Justus *et. al.* demonstrated this effect using Nigrosin dye dissolved in CS_2 and either a roughened glass surface or a suspension of microscopic glass fibers as the scatterer. Both systems showed an improvement of limiting over the thermal defocusing effect of the Nigrosin alone. A similar method, but using thermally induced coherent scattering has been proposed using an absorbing, index-matched dye solution in a photonic bandgap nanochannel glass.[5] Here we report on a nonlinear scattering optical limiter that uses a highly porous sol-gel glass as the scattering medium, into which we diffuse reverse saturable absorber dyes dissolved in an index-matched solvent to produce limiting by a combination of nonlinear absorption and nonlinear scattering.

2. EXPERIMENTAL PROCEDURE

Highly porous sol gel glass samples were fabricated and formed into discs of approximately 0.9 mm thickness and 5 mm diameter. In these samples 24% of the free volume is SiO_2 glass, the remaining 76% being occupied by pores of average diameter 200Å. In their dry state, these discs are whitish with a blue tint in their appearance due to their strong broadband optical scattering properties. For experimental measurements, the discs were placed in 1 mm path length spectroscopic cells filled with index matching fluid into which a dye was dissolved. The solvent 2-methylcyclohexanol was found to give the best index matching. We originally attempted to use Nigrosin dye, which exhibits very small nonlinearities, permitting observation of the thermally induced refractive index effects without the complications of other nonlinear effects.[4] However, we were unable to attain good index matching using Nigrosin in 2-methylcyclohexanol. Instead, we used several dyes that exhibit reverse-saturable absorption (RSA) and hence produce a substantial intrinsic limiting effect. However, it is relatively simple to distinguish intrinsic limiting due to RSA from nonlinear scattering in the sol gel by comparing limiting in the disc with limiting in the solvent alone.

The limiting measurements were carried out using 7 ns (FWHM) laser pulses at 532 nm, obtained by second harmonic generation of an injection-seeded Q-switched Nd:YAG laser running at a 10Hz repetition rate. We used an *f*/15 focusing

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Part of the SPIE Conference on Power-Limiting Materials and Devices
Denver, Colorado • July 1999
SPIE Vol. 3798 • 0277-786X/99/$10.00

geometry with a near-Gaussian input beam and the transmitted light was imaged onto a large-area silicon photodiode using *f*/4.5 collection optics. A schematic of the experimental system is shown in Fig. 1. The input energy was monitored using a calibrated photodiode and data from both detectors was collected by computer via A/D converters. A half-wave plate and polarizer arrangement was used to vary the input energy and the transmittance of the limiter was measured as a function of the input energy.

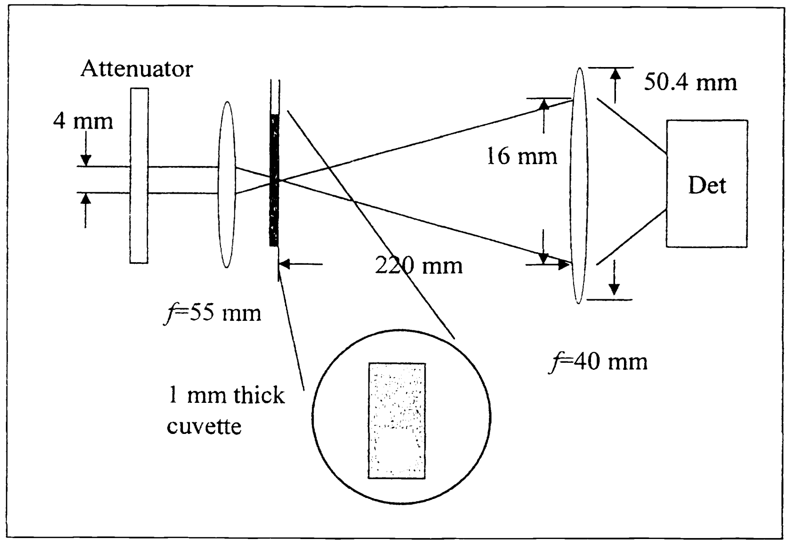

Figure 1. Schematic of the optical limiting measurement system.

3. RESULTS AND DISCUSSION

The first solution that we found to produce good index matching was iodine in 2-methylcyclohexanol. Although this was chosen for its broadband linear absorption, our results indicate that this material also has attractive RSA properties. Figure 2 below shows the transmittance as a function of input energy for a porous solgel disc index-matched with iodine in 2-methylcyclohexanol. For comparison, the transmittance was also measured in the solvent but outside the disc.

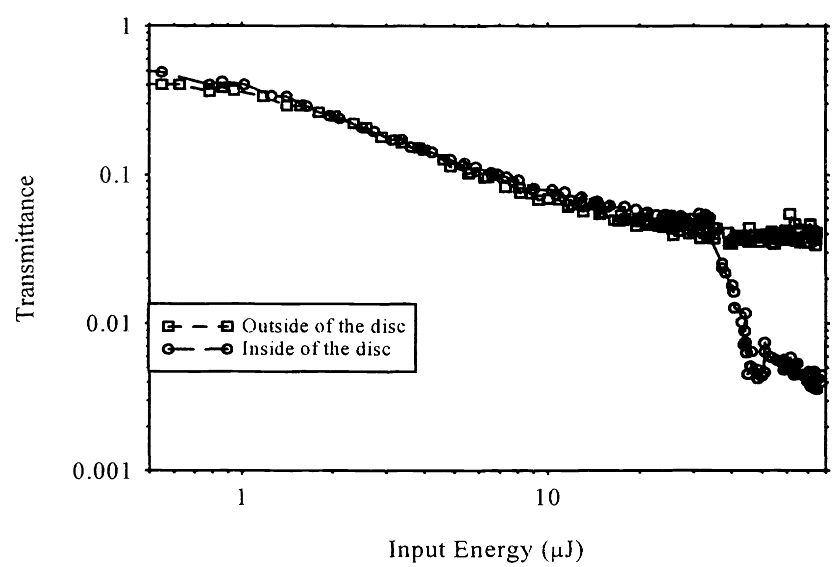

Figure 2. Transmittance versus input energy for porous solgel index-matched with iodine in 2-methylcyclohexanol. The linear transmittance is 64%.

From Fig. 2, we clearly see that the effect of the porous glass is to enhance the limiting at higher energies, although this enhancement occurs with a surprisingly sharp energy threshold, at about 35 μJ input energy. This sharp change in transmittance is reversible, and hence not associated with damage, as will be discussed below. A strong increase in side scattered light was observed, confirming that the effect is due to nonlinear scattering, as expected. Permanent, irreversible damage was observed in this sample at an input energy of approximately 100 μJ. The overall figure of merit (FOM),[6] defined as the ratio of linear transmittance to minimum transmittance, for this device is approximately 170. However, as revealed in Fig. 3, because of the sharp limiting threshold the maximum transmitted energy occurs just below the threshold for nonlinear scattering and not at the maximum incident energy, so the FOM is not a complete measure of the limiting performance in this particular case.

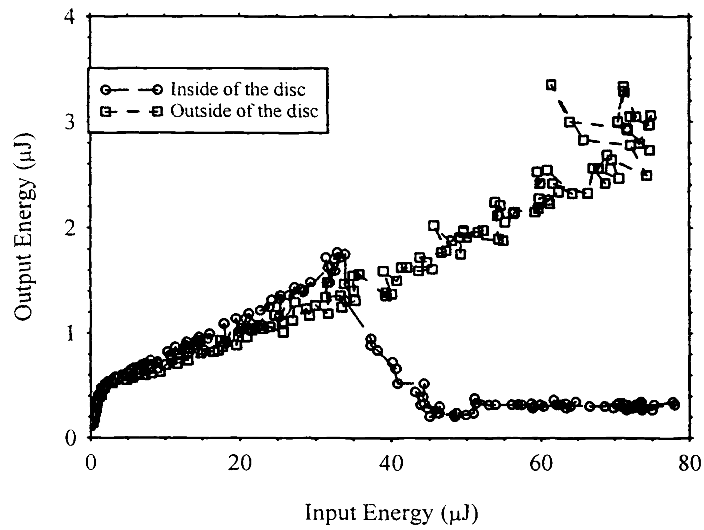

Figure 3. Data of figure 2, plotted as output energy vs. input energy.

Similar behavior was observed using t-butyl zinc phthalocyanine (ZnPc) dissolved in 2-methylcyclohexanol. In this case, strong limiting was observed with a sample with internal linear transmittance of 94%, as shown in Fig. 4. In this case, the threshold for nonlinear scattering is less sharp. The maximum transmitted energy is 3 μJ.

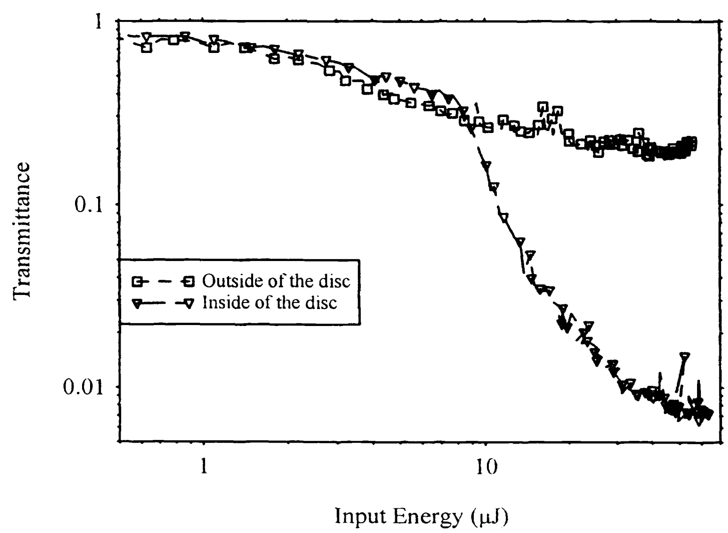

Figure 4. Nonlinear transmittance for porous glass index-matched with ZnPc in 2-methylcyclohexanol

Our original simple model of thermal index changes in the solvent would have led us to expect a more gradual threshold for nonlinear scattering than is observed. Further inadequacies of this model are revealed by longer-term studies of the limiting. In Fig 5., we show the results of repetitively measuring the energy dependence of transmittance at the same spot on the sample. The sample is the iodine sample of Figs. 2 and 3. Each data point corresponds to measurement of a single laser pulse, although as the pulse repetition rate is 10 Hz, there are about 5 – 10 pulses incident on the sample between each recorded data point. Clearly, the limiting effect is reversible in the sense that each time we go back to low energy, the original linear transmittance is recovered. However, after a few limiting runs, the nonlinear scattering effect gradually disappears. We also find that there is an aging effect, in that the nonlinear scattering disappears a few hours after preparing the sample. This is shown in Fig. 6.

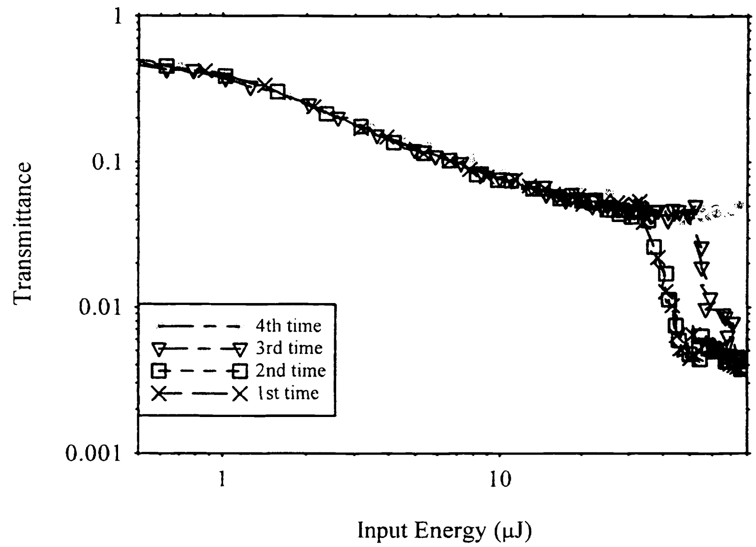

Figure 5. Results of repetitive measurements of nonlinear transmittance at 10 Hz repetition rate at a single position in the iodine / 2-methylcyclohexanol sample.

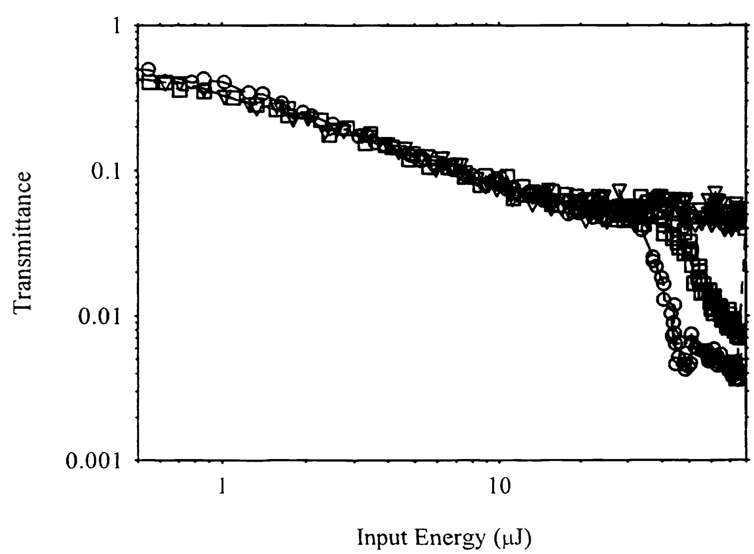

Figure 6. Results of measurement of the nonlinear transmittance of iodine in 2-methylcyclohexanol sample. Circles - freshly-prepared sample. Squares - 2 hours later. Triangles - one day later.

These long-term effects indicate that the nonlinear scattering is not explained by the simple thermal mechanism originally proposed. Moreover, experiments at very low repetition rate show that the nonlinear scattering is quite ineffective on a single laser shot. By illuminating a fresh point on the sample at high energy and measuring the transmittance as a function of number of laser shots, we find that it takes 30-50 shots at 10 Hz for the nonlinear scattering to attain its full effect. Also, if we turn down the laser energy immediately after observing the strong nonlinear scattering, we observe the shadows of bubbles within the transmitted beam. These are observed to slowly move out of the beam or dissipate on a time scale of approximately 1 minute after reducing the energy.

These observations indicate that the nonlinear scattering may be primarily due to bubble formation. This would explain the sharp threshold and the bubbles observed. The calculated temperature at the threshold for nonlinear scattering is less than the boiling point for 2-methylcyclohexanol. However, the porous glass matrix will provide many nucleation centers for bubbles. However, this model alone does not adequately explain the aging effects. The laser intensity and temperature rise are too low to attribute the disappearance of nonlinear scattering after many shots to annealing of the glass, and the glass seems to be stable in the 2-methylcyclohexanol. However, it could be that gases are absorbed into the surface of the glass pores. These could cause bubbles to form on laser heating and the aging effect could be due to dissolution of the gas into the solution and diffusion out of the glass disc. Another possibility is that very tiny bubbles are trapped in the pores of the glass. If these are small enough, they may cause insignificant amounts of scatter. However, they may grow under laser heating, producing strong scattering. The aging effect can be again explained by gradual dissolution of the gas into the solvent.

We often found problems of repeatably obtaining the nonlinear scattering effect in our experiments. The effect seems to depend strongly on the position within the sample. To test this, we measured the low energy transmittance of a dry porous glass sample at focus in our limiting setup while moving the sample across the beam. We found that the transmittance varies from a few percent to about 50 %. Hence, the porous glass is not sufficiently uniformly scattering and the uniformity needs to be improved upon to produce a reliable limiter.

4. CONCLUSIONS

These experiments have revealed a potentially useful limiting effect in an index matched solgel glass. The strength of the limiting effect is impressive for a single element. However, the mechanism needs further study to find ways to eliminate the aging effects and the solgel glasses need to be modified to be more uniformly scattering. The cumulative nature of the limiting effect need not be a problem, however. Although this is a drawback to using this device alone as a sensor protector, it is an extremely useful complement to another limiter, "carbon black suspension" (dilute ink) that limits very well on a single shot, but not on subsequent shots.[1] A hybrid device that incorporates both porous glass and carbon black nonlinear scattering elements could be an attractive option for sensor protection.

ACKNOWLEDGEMENTS

This work was carried out under the support of the I-4 Corridor High Technology Consortium and the Naval Air Warfare Center Joint Service Agile Program (contract number N00421-98-C-1327). Carrol Basañez acknowledges the support of the National Science Foundation through the Research Experiences for Undergraduates program at the University of Central Florida (Grant NumberEEC9732420)

REFERENCES

1. "Nonlinear optical properties of carbon-black suspensions (ink)", K. Mansour, M. J. Soileau, and E. W. Van. Stryland, JOSA B, 9, 1100 (1992).
2. "Nonlinear optical effects in carbon suspensions", K. J. McEwan, P. K. Milsom, and D. B. James, Proc. SPIE, 3472, 42 (1998).
3. "Nonlinear Optical Properties of Inorganic Metallic Clusters", T. Xia, A. Dogariu, K. Mansour, D.J. Hagan, A.A. Said, E.W. Van Stryland and S. Shi, JOSA B, 15, 1497 (1998).
4. "Thermal-defocusing/scattering optical limiter", B. L. Justus, A. J. Campillo, and A. L. Huston, Opt. Lett. 19, 674 (1994).
5. "Two-dimensional photonic bandgap optical limiter in the visible", H-B, Lin, R. J. Tonucci, and A. J. Campillo, Opt. Lett. 23, 94 (1998).
6. "Optimization of optical limiting devices based on excited-state absorption", T. Xia, D. J. Hagan, A. Dogariu, A. A. Said, and E. W. Van Stryland, Appl. Opt. 36, 4110 (1997).